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Highlights

| Liquid liquid equilibria of binary systems (bonzone + [x Mim][NTf ] ionis liquid);                      | Fluid Phase Equilibria xxx (2013) xxx-xxx |
|---|---|
| Experimental data and thermodynamic modeling using a group contribution equation                        | of state                                  |
| Emilio J. González, Susana B. Bottini, Selva Pereda, Eugénia. A. Macedo*                                |   |
| • Mutual solubilities of binary mixtures {benzene+ionic liquid} were measured.                          |   |
| • The experimental LLE data were modeled using the GC-EoS equation.                                     |   |
| • The GC-EOS was applied to predict LLE and VLE of {benzene + <i>x</i> -MimNTf <sub>2</sub> } mixtures. |   |
| • The GC-EOS was used to predict LLE of {hexane + benzene + [x-Mim][NTf <sub>2</sub> ]} mixtures.       |   |
| • CC EQS is canable of predicting the phase behavior of these mixtures                                  |   |

• GC-EOS is capable of predicting the phase behavior of these mixtures.

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### Fluid Phase Equilibria



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### Liquid,-liquid equilibria of binary systems {benzene + [x-Mim][NTf<sub>2</sub>] ionic liquid}: Experimental data and thermodynamic modeling using a group contribution equation of state

### Q1 Emilio J. González<sup>a</sup>, Susana B. Bottini<sup>b</sup>, Selva Pereda<sup>b</sup>, Eugénia. A. Macedo<sup>a,\*</sup>

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#### ARTICLE INFO

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Article history: Received 15 July 2013 Received in revised form 19 September 2013 Accepted 21 September 2013 Available online xxx Keywords: 1-Alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ionic liquids Benzene Liquid–liquid equilibria Group-contribution equation of state

### ABSTRACT

Furthermore, the group contribution equation of state (GC-EoS) was applied to model the phase behavior of mixtures of hydrocarbons with different members of the homologous family 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [x-Mim][NTf<sub>2</sub>]. New pure group parameters for the ionic liquid functional group (MimNTf<sub>2</sub>) and interaction parameters between this group and the paraffin (CH<sub>3</sub>, CH<sub>2</sub>) and aromatic (ACH) groups are reported. The GC-EOS extended with the new parameters was applied to predict LLE and VLE of binary mixtures {benzene + x-MimNTf<sub>2</sub>} and LLE of ternary systems {n-hexane + benzene + [x-Mim][NTf<sub>2</sub>]}. The results show that the GC-EOS is capable of predicting the phase behavior of this kind of mixtures with reasonable accuracy.

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#### 1. Introduction

Ionic liquids (ILs) are a relatively new class of molten salts with many interesting properties that makes them a potential replacement for classic organic solvents. In contrast to common molten salts, they are in the liquid state at temperatures below 373 K. Their unique properties (mainly their non-volatile nature, high capacity to dissolve organic and inorganic compound, and easy recovery) have originated an enormous interest in the scientific community and they are being applied in many fields [1]. Furthermore, their properties can be modified by varying the chemical structure of the cation and/or anion, allowing the design of new ILs for specific applications.

In the last decade, the use of ILs as solvents for the separation of aromatic from aliphatic hydrocarbons has been one of the most widely studied applications of ILs, as reflected in recent reviews published in the literature [2–4]. In this respect, knowledge of liquid, liquid equilibrium (LLE) conditions of alkanes + aromatic hydrocarbons + ILs mixtures is required. The need is for both, experimental data and adequate thermodynamic models able to

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represent the phase boundaries and distribution coefficients of aromatic and aliphatic hydrocarbons at equilibrium.

Many researchers have studied the mutual solubility of ILs and hydrocarbons [5–14] and additional information is continuously being published as new ILs are being synthesized.

In this paper, LLE experimental data for two (ionic liquid + benzene) binary mixtures have been measured at  $T_{\wedge} = (293.15 - 333.15)$ K and atmospheric pressure. The ILs studied were 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMim][NTf<sub>2</sub>]) and 1hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([HMim][NTf<sub>2</sub>]). The experimental results are in good agreement with those previously reported in *literature* [5,8] for the same systems.

As mentioned before, one advantage of ILs is the almost unlim-59 ited number of compounds that can be designed by combining 60 different ions. However, this benefit involves an enormous exper-61 imental effort, due to the large number of mixtures that should 62 be studied. In this respect, adequate thermodynamic models can 63 help in making a preliminary screening of suitable ILs for specific 64 applications. Well-known Gibbs free energy models such as Non 65 Random Two-Liquids (NRTL), electrolyte NRTL (e-NRTL), and Uni-66 versal Quasichemical (UNIQUAC) models were used to describe 67 phase behavior of systems containing ILs [15–17]. Usually, these

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equations are used in their purely correlative manner. Therefore, thermodynamic modeling of the considered systems by using predictive tools still remains an almost unexplored field. Nowadays, one of the most accepted models for predicting the thermodynamic properties of ILs is the conductor-like screening model for real solvents (COSMO-RS). This model, based on the quantum chemical description of individual molecules, was successfully applied for the prediction of solubility of mixtures containing hydrocarbons and ionic liquids [18]. The modified UNIFAC for systems with ILs is another model that has recently become very popular because of its applicability for prediction of thermodynamic properties of binary mixtures containing this kind of molten salts [19–21].

Equations of state (EoS) have also proven to be very powerful tools to describe the properties of pure fluids or their mixtures. In the last 10 years, this kind of models has been widely applied to describe the properties of pure ILs, as well as to model the phase behavior of mixtures containing them. Classical cubic equations like Peng-Robinson (PR) or Soave-Redlich-Kwong (SRK), or others like Statistical Associating Fluid Theory (SAFT)-type equations which take into account the structure of the molecule, have been used to model the phase behavior of systems containing ILs [22–26]. Recently, the Cubic Plus Association (CPA) equation of state, which combines the SRK EoS with an association term similar to that of the SAFT type models, has been also applied to describe the phase behavior of several ionic liquids, with very successful results [27,28]. More detailed information about the applicability of EoS and related models to the thermodynamics of ILs can found in the recent review published by Maia et al. [27].

In this work, the group-contribution equation of state GC-EoS [29,30] was used to represent the phase behavior of binary and ternary mixtures containing benzene, n-hexane and 1-alkyl-3methylimidazolium bis(trifluoromethylsulfonyl)imide. This equation has already been applied to calculate the solubility of carbon dioxide in ILs at high pressures [31,32]. For a given cation, anion combination, the properties of the different members of the same family of ILs are calculated by changing the length of the alkyl chain normally attached to the cation; i.e., every IL is represented by a given cation-anion functional group plus a certain number of alkyl radicals. In this particular case, the benzene + nhexane + [x-Mim][NTf<sub>2</sub>] mixtures were represented by the ionic liquid functional group (MimNTf<sub>2</sub>), plus the paraffin (CH<sub>3</sub>, CH<sub>2</sub>) and aromatic (ACH) groups. The equation was applied to correlate and predict the experimental data measured in this work and also vapor\_liquid (VLE) and liquid\_liquid (LLE) equilibria for binary and ternary mixtures reported in literature [33–35].

#### 2. Experimental

#### 2.1. Chemicals

Benzene, with a mass fraction purity higher than 0.999, was purchased from Sigma<sub>A</sub>-Aldrich; it was degassed ultrasonically and dried over molecular sieves of  $4 \times 10^{-8}$  cm supplied by the same company. After this treatment, it was kept in a bottle under inert atmosphere.

The ILs used in this work were supplied by lolitec GmbH (Germany) with a mass fraction purity higher than 0.99. Prior to their use, they were subjected to vacuum ( $p = 2 \times 10^{-1}$  Pa) at moderate temperature (T = 343.15 K) for several days in order to reduce moisture and any residual solvent. They were also kept under argon atmosphere. The water content of the ILs was determined with a Karl Fisher titrator (Metrohm 870 KF Titrino) using Titran 2, supplied by Merck, as titrant. The values determined in [EMim][NTf<sub>2</sub>] and [HMim][NTf<sub>2</sub>] were 600 and 614 ppm, respectively.

#### 2.2. Apparatus and procedure

Experimental LLE data were obtained by the following proce-131 dure: an immiscible {benzene+ionic liquid} binary mixture was 132 introduced inside a glass cell, and sealed using a silicon cover. To 133 ensure an intimate contact between both phases, the mixture was 13/ vigorously stirred for 3 h, It was then left for at least 3 h in a ther-135 mostatic bath (PoliScience digital temperature controller, with a 136 stability of  $\pm 0.01$  K) in order to ensure thermodynamic equilibrium. 137 The temperature was controlled using a digital thermometer (ASL 138 model F200) with an uncertainty of  $\pm 0.01$  K. Next, a sample from 139 each phase was withdrawn using a syringe and its density was mea-140 sured at T = 283.15 K in a digital vibrating tube densimeter (Anton 141 Paar DSA-5000 M). The compositions of both phases were deter-142 mined using calibration curves, which were previously obtained 143 by measuring the density of miscible (benzene + IL) mixtures with 144 known composition [36]. This procedure was repeated for each 145 temperature. Samples were prepared in duplicate in order to calcu-146 late the uncertainty in the determination of the composition. From 147 the results obtained, the estimated error in the mole fraction is less 148 than +0.005.

#### 3. Thermodynamic modeling

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As it was already mentioned, the phase behavior of the binary mixtures {benzene + ionic liquid} was modeled with the GC-EoS equation [29,30]. The basis of this equation is the generalized van der Waals partition function, combined with the local composition principle. It is expressed in terms of the residual Helmholtz energy (A<sup>R</sup>) as the addition of an attractive term (att) and a free volume (fv) contribution:

$$\left(\frac{\underline{A}^{R}}{RT}\right)_{T,V,n} = \left(\frac{\underline{A}^{R}}{RT}\right)_{att} + \left(\frac{\underline{A}^{R}}{RT}\right)_{f\nu}$$
(1) 15

The free volume term is described by the Mansoori and Leland expression for hard spheres:

$$\left(\frac{A^{R}}{RT}\right)_{f\nu} = 2\left(\frac{\lambda_{1}\lambda_{2}}{\lambda_{3}}\right)(Y-1) + \left(\frac{\lambda_{2}^{3}}{\lambda_{3}^{2}}\right)(Y^{2}-Y-\ln Y) + nLnY \quad (2)$$
<sup>16</sup>

with  $\lambda_k = \sum_j^{NC} n_j d_j^k$  and  $Y = (1 - \pi \lambda_3/6V)^{-1}$  where *n*, *NC*, *V* and *d*, are the total number of moles, the number of components, the total volume and the hard-sphere diameter per mole, respectively.

The hard-sphere diameter d is assumed to be temperaturedependent and is described by the following expression:

$$d = 1.065655d_c \left( \frac{1 - 0.12 \exp\left(\frac{-2T_c}{3T}\right)}{3T} \right)$$
(3) 16

where  $d_c$  is the value of the hard-sphere diameter at the critical temperature  $T_c$  for the pure component.

The attractive term is a group contribution version of a density dependent NTRL expression: 171

$$\begin{pmatrix}
\frac{A^{R}}{RT}
\end{pmatrix}_{att} = -\frac{\left(\frac{z}{2}\right)\sum_{i=1}^{NC}n_{i}\sum_{j=1}^{NG}\upsilon_{j}^{i}q_{j}\sum_{k=1}^{NG}\theta_{k}(q_{kj}\tilde{q}\tau_{kj}/RTV)}{\sum_{l=1}^{NG}\theta_{l}\tau_{lj}}$$
(4) 17.

where

$$\theta_{k} = \left(\frac{q_{k}}{\tilde{q}}\right) \sum_{i=1}^{NC} p_{i} \upsilon_{k}^{i} \qquad \tilde{q} = \sum_{i=1}^{NC} p_{i} \sum_{j=1}^{NG} \nu_{j}^{j} q_{j}$$
(5) 17

$$\Delta g_{kj} = g_{kj} - g_{jj} \tag{7}$$

In Eq. (4), *z* is the number of coordination (set equal to 10);  $v_i^i$  is the number of times group *j* appears in molecule *i*;  $q_i$  is the 178

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number of surface segments assigned to group *j*;  $\theta_k$  is the surface fraction of group *k*;  $\tilde{q}$  is the total number of surface segments in the mixture;  $g_{jj}$  is the attractive energy parameter for interactions between segments *j* and *i*; and  $\alpha_{jj}$  is the corresponding nonrandomness parameter.

The interactions between unlike segments are defined by:

$$g_{ji} = k_{ji} \sqrt{g_{ii}g_{jj}} \tag{8}$$

where k<sub>ij</sub> is a binary interaction parameter. The following temperature dependences are assumed for the attractive energy parameter and the binary interaction parameters:

$$g_{ii} = g_{ii}^{*} \left[ 1 + g_{ii}' \left( \frac{\overline{X}}{T_{i}^{*} - 1} \right) + g_{ii}'' \ln \left( \frac{\overline{X}}{T_{i}^{*}} \right) \right]$$
(9)  
$$k_{ij} = k_{ij}^{*} \left[ \mathbf{1} + k_{ij}' \ln \frac{\overline{X}}{T_{ij}^{*}} \right]$$
(10)

$$\frac{T_{ii}^* = 0.5(T_i^* + T_i^*)}{(11)}$$

where  $T_i^*$  is the reference temperature of group i.

#### 193 3.1. Ionic liquid functional group

In order to apply the GC-EoS, the pure components were represented by the corresponding functional groups. Benzene was represented by six aromatic (ACH) functional groups, n-hexane by two (CH<sub>3</sub>) and four (CH<sub>2</sub>) alkyl groups and the ILs were decomposed into the (MimNTf<sub>2</sub>) group (cation + anion core), plus the corresponding number of (CH<sub>2</sub>) and (CH<sub>3</sub>) groups in the side alkyl chain, as shown in Fig. 1 [32].

#### 3.1.1. Parameterization of the free volume term

The free volume term is characterized by the critical hard-sphere diameter  $d_c$ . Usually, this parameter is calculated from the critical properties of the pure component, or by fitting the equation to some point of the vapor pressure curve. Since ILs present negligible vapor pressures at normal conditions, an alternative method should be used for these compounds. In this work the  $d_c$  value of ILs was calculated from information on the molar volume of the pure component.

Pereda [37] found the following correlation between the molar volumes  $V_m$  (cm<sup>3</sup>/mol) of pure ionic liquids and their van der Waals volumes  $r_{VdW}$ :

$$r_{VdW} = 0.04 \cdot V_m \tag{12}$$

From the van der Waals volumes, the critical diameter  $d_c$  of the pure ILs was then calculated using the equation proposed by Espinosa et al. [38] for high molecular weight compounds:

$$\log_{10} d_{\rm c} = 0.4152 + 0.4128 \log_{10} r_{VdW}$$
(13)

The values of the critical diameters of [EMim][NTf<sub>2</sub>] and [HMim][NTf<sub>2</sub>] calculated with this procedure, were equal to 6.826 cm/mol and 7.510 cm/mol, respectively

http://dx.doi.org/10.1016/j.fluid.2013.09.048

### Table 1

Experimental LLE data for the binary mixtures {benzene (1)+ionic liquid (2)} at different temperatures, expressed as mole fraction of benzene,  $x_1$ .

| T/K    | <i>x</i> <sub>1</sub>     |                           |  |  |
|--------|---------------------------|---------------------------|--|--|
|        | [EMim][NTf <sub>2</sub> ] | [HMim][NTf <sub>2</sub> ] |  |  |
| 293.15 | 0.7762                    | 0.8771                    |  |  |
| 298.15 | 0.7723                    | 0.8769                    |  |  |
| 303.15 | 0.7733                    | 0.8757                    |  |  |
| 308.15 | 0.7730                    | 0.8750                    |  |  |
| 313.15 | 0.7694                    | 0.8748                    |  |  |
| 318.15 | 0.7709                    | 0.8768                    |  |  |
| 323.15 | 0.7698                    | 0.8777                    |  |  |
| 328.15 | 0.7656                    | 0.8779                    |  |  |
| 333.15 | 0.7667                    | 0.8825                    |  |  |

#### 3.1.2. Parameterization of the attractive term

The following parameters are required to calculate the attractive term of the GC-EoS:

- Pure group constants:  $T_{ii}^*, q_i$  224
- Pure group energy parameters:  $g_{ii}^*g_{ij}'g_{ii}''$

- Group, group interaction parameters:  $k^*$ ,  $k'_{ij}$ ,  $\alpha_{ij}$ ,  $\alpha_{ji}$ 

The pure group constants and parameters of the ACH,  $CH_3$  and  $CH_2$  groups and the binary parameters for the interactions between these groups were taken from literature [30].

The surface area  $q_i$  of the (MimNTf<sub>2</sub>) functional group was calculated from the van der Waals area of the ionic liquid molecule:

$$q_{VdW} = \frac{z-2}{z} r_{VdW} + \frac{z}{2}$$
(14) 232

after subtracting from this value the surface area of the side alkyl chain attached to the imidazolium cation [37].

The characteristic temperature  $T_i^*$  for the (MimNTf<sub>2</sub>) group was fixed at the usual value of 600 K [30].

Pure group energy parameters and binary interaction parameters of this group with the alkyl functional groups (CH<sub>3</sub>), (CH<sub>2</sub>) were obtained by adjusting infinite dilution activity coefficients of alkanes [37]. The binary interaction parameters ( $k_{ij}$  and  $\alpha_{ij}$ ) between (MimNTf<sub>2</sub>) and the aromatic (ACH) group were determined by adjusting the experimental LLE data reported in this work for the binary mixtures {benzene+[EMim][NTf<sub>2</sub>] or [HMim][NTf<sub>2</sub>]} and VLE data for the binary system {benzene+[BMim][NTf<sub>2</sub>]} taken from [iterature [33].

#### 4. Results and discussion

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#### 4.1. {Benzene + [x-Mim]NTf<sub>2</sub>]} binary mixtures

The experimental LLE data for the binary mixtures {benzene  $(1)+[EMim][NTf_2]$ , or  $[HMim][NTf_2]$  (2)} are reported in Table 1 in terms of the mole fraction of benzene in the IL-rich phase. The IL was considered to be immiscible in the hydrocarbon phase in the range of temperatures studied. Benzene mole fraction in the IL phase increases about 15% when the side alkyl chain in the IL changes from ethyl to hexyl. It becomes clear that the increase of the alkyl chain length leads to a lower polarity of the ionic liquid and a higher free volume, which enhances solubility of the aromatic [18]. Within the temperature range studied in this work, benzene solubility remains almost constant, with a slight tendency to decrease with temperature, particularly for [EMim][NTf\_2].

Fig. 2 shows the results of the experimental measurements. For comparison, data from <u>literature [5,8]</u> for the same systems are also included in the figure.

These experimental LLE data, together with information on VLE of {benzene + [BMim][NTf<sub>2</sub>]} taken from **lit**erature [33], were used

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 $\label{eq:Fig_A2} \begin{array}{l} \text{Experimental LLE data of the binary systems } \{ \texttt{benzene (1)+ionic liquid (2)} \}. \\ \text{Symbols are experimental data: } (\Box) [\texttt{EMim}[\texttt{NTf}_2] (\texttt{this work}); (\bigcirc)[\texttt{HMim}]][\texttt{NTf}_2] (\texttt{this work}); (\bigcirc)[\texttt{HMim}[\texttt{NTf}_2] (\texttt{Ref}, [5]); (\times) [\texttt{EMim}[\texttt{NTf}_2] (\texttt{Ref}, [8]); (\bullet) [\texttt{HMim}[\texttt{NTf}_2] (\texttt{Ref}, [5]). \\ \texttt{Lines represent GC-EoS correlation of experimental data: } (-)[\texttt{EMim}][\texttt{NTf}_2] \\ \texttt{and } (-) [\texttt{HMim}][\texttt{NTf}_2]. \end{array}$ 

#### Table 2

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GC-EoS pure-group parameters.

| Group           | $T^*/K$ | q     | <i>g</i> * | g'      | <i>g</i> ″ | Source |
|-----------------|---------|-------|------------|---------|------------|--------|
| [Mim][NTf2]     | 600     | 7.098 | 501325     | 0.9006  | 0.0000     | [37]   |
| ACH             | 600     | 0.4   | 723210     | -0.606  | 0.0000     | [30]   |
| CH <sub>3</sub> | 600     | 0.848 | 316910     | -0.9274 | 0.0000     | [30]   |
| CH <sub>2</sub> | 600     | 0.54  | 356080     | 0.8755  | 0.0000     | [30]   |

to fit the interaction parameters between the aromatic ACH and the ionic liquid [mim][NTf<sub>2</sub>] functional groups of the GC-EoS equation. The values of the new parameters, together with all pure group and binary interaction parameters used in the calculations, are reported in Tables 2 and 3.

Even though it was possible to obtain a good correlation and prediction of the experimental VLE data (see Fig<sub>A</sub> 3), the solubility of benzene in [EMim][NTf<sub>2</sub>] and [HMim][NTf<sub>2</sub>] calculated by the GC-EoS was only qualitatively correct and the equation was not able to follow the temperature dependence shown by the experimental data (see Fig<sub>A</sub> 2).

## 4.2. Effect of temperature on LLE of {benzene + [x-Mim][NTf<sub>2</sub>]} systems

Lachwa et al. [5] studied the influence of the cation alkyl chain length on the liquid\_liquid phase split of {benzene+[x-Mim][NTf<sub>2</sub>]} binaries, by measuring LLE up to 480 K. They found that, as the side alkyl chain increases from ethyl to hexyl, the immis-

| Table 3       |             |            |
|---------------|-------------|------------|
| GC-EoS binary | interaction | parameters |

| i                        | j               | $k^*$  | $k'_{ij}$ | $\alpha_{ij}$ | $\alpha_{\rm ji}$ | Source    |
|--------------------------|-----------------|--------|-----------|---------------|-------------------|-----------|
| [Mim][NTf <sub>2</sub> ] | CH₃             | 0.7238 | 0.000     | 4.050         | 1.7185            | [37]      |
| [Mim][NTf <sub>2</sub> ] | $CH_2$          | 0.7656 | 0.000     | 4.050         | 1.7185            | [37]      |
| [Mim][NTf <sub>2</sub> ] | ACH             | 0.9014 | -0.1224   | -5.4880       | -10.5596          | This work |
| ACH                      | CH <sub>3</sub> | 1.041  | 0.0944    | 0.3915        | 0.3915            | [30]      |
| ACH                      | $CH_2$          | 1.041  | 0.0944    | 0.3915        | 0.3915            | [30]      |
| CH <sub>3</sub>          | $CH_2$          | 1.000  | 0.0000    | 0.0000        | 0.0000            | [30]      |



**Fig**<sub>A</sub> **3.** (a) VLE of the binary system {benzene (1)+[BMim][NTf<sub>2</sub>] (2)} at 353 K. ( $\Box$ ) Exp. [33]; (-) GC-EoS correlation. (b) VLE of the binary system {benzene (1)+[EMim][NTf<sub>2</sub>] (2)}. ( $\bigcirc$ ) Exp. [33]; (-) GC-EoS prediction.

cible region reduces significantly. The phase diagram of these ILs 282 adopts the so-called 'hourglass' shape. A further increase of the 283 alkyl chain to octyl and decyl, enhances the mutual solubility even 284 more and induces the disengagement of the upper (UCST) and lower 285 (LCST) critical solution temperatures. For octyl [OMim][NTf<sub>2</sub>] and 286 decyl [DMim][NTf<sub>2</sub>] ionic liquids, the UCST is located at about 370 K and 320 K, respectively, while the LCST displaces to temperatures 288 higher than 500 K [5]. 289

Fig<sub>x</sub> 4 shows the LLE phase diagrams predicted by the GC-EoS equation for the binaries {benzene +  $[x_{T}Mim][NTf_2]$ } ionic liquids with *x* = butyl, octyl and decyl.

For all these systems, the GC-EoS model predicts the existence of an UCST. As shown in  $Fig_{A}^{4}$ , the performance of the equation improves as the side alkyl chain length in the IL increases.

The COSMO-RS model has also been applied to calculate the LLE phase diagrams of different families of ILs [18]. Similarly to the GC-EoS equation, for the {benzene+[ $x_x$ Mim][NTf<sub>2</sub>]} systems this 298

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**Fig**<sub>A</sub> **4.** Experimental LLE data of the binary systems {benzene (1)+ionic liquid (2)}. Lines are GC-EoS predictions: (-) [BMim][NTf<sub>2</sub>]; (-) [OMim][NTf<sub>2</sub>] and (-) [DMim][NTf<sub>2</sub>]. Symbols: Experimental data (ref. [5]) ( $\bullet$ ) [BMim][NTf<sub>2</sub>];  $(<math>\bullet$ ) [OMim][NTf<sub>2</sub>];  $(\times)$  [DMim][NTf<sub>2</sub>].

model predicts the existence of UCSTs. However, in this case the
values of the calculated UCSTs are much lower than the experimental data. The COSMO-RS model predicts complete miscibility
for all these systems at temperatures above ambient [18].

#### 4.3. LLE of ternary {n-hexane + benzene + [xMim][NTF<sub>2</sub>]} systems

The GC-EoS equation was also applied to predict LLE of ternary mixtures containing *n*-hexane, benzene and [*x*-Mim][NTf<sub>2</sub>] ionic liquids. A comparison between experimental [34,35] and predicted data for the ternary systems {*n*-hexane (1)+benzene (2)+[EMim][NTF<sub>2</sub>], or [BMim][NTf<sub>2</sub>], or [Omim][NTf<sub>2</sub>] ionic liquid (3)} are depicted in Fig. 5.

Moreoever, benzene distribution coefficient ( $\beta$ ) and selectivity (*S*):

$$\beta = \frac{x_2^{ll}}{x_2^{l}}$$

$$S = \frac{x_2^{ll} x_1^{l}}{x_2^{l} x_1^{ll}}$$

$$(15)$$

are also plotted in Fig. 6.  $x_1^l$  and  $x_2^l$  are the mole fraction of hex-314 ane and benzene, in the upper phase (hydrocarbon-rich phase), 315 respectively; and  $x_1^{ll}$  and  $x_2^{ll}$  are the mole fraction of hexane and 316 benzene, in the lower phase (IL-rich phase), respectively. From Figs. 317 5 and 6, it is possible to observe that the size of the alkyl chain 318 length of the cation has as important effect on the LLE data. For this 319 kind of ternary mixtures which are type 2 according to the classi-320 fication proposed by SØrensen et al. [39], the immiscibility region 321 decreases with the increase of the cation size alkyl chain length. 322 The tie-lines, and therefore the selective and solute distribution 323 ratio, also depend on the alkyl chain length. The selectivity values 324 decrease as the cation alkyl chain increases while the solute distri-325 bution ratio increases with the alkyl chain length. A dependence of 326 S and  $\beta$  values with the aromatic content is also observed, showing 327 a decrease of these parameters with the content of benzene in the 328 hydrocarbon-rich phase. 329

From these figures, it is also possible to observe that GC-EoS model predicts very satisfactorily the experimental trends obtained







**Fig. 5.** Experimental and predicted LLE data for the ternary systems {hexane (1)+benzene (2)+[x-Mim][NTf<sub>2</sub>] ionic liquid} at 298 K: (a) [EMim][NTf<sub>2</sub>] [35]; (b) [BMim][NTf<sub>2</sub>] [34]; (c) [OMim][NTf<sub>2</sub>] [34]. Solid lines and full points represent experimental tie-lines; dashed lines and empty squares are GCA-EoS predictions.

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Fig. 6. (a) Selectivity and (b) benzene distribution ratio for the ternary systems {hexane (1) + benzene (2) + [x-Mim][NTf<sub>2</sub>] ionic liquid}. Lines are GC-EoS predictions. Symbols: experimental data () [EMim[NTf2] (Ref. [35]); () [BMim]][NTf2] (Ref. [34]); () [OMim[NTf2] (Ref. [34]).

for binodal curves, tie-line slopes, and *S* and  $\beta$  values and it can be successfully used as a tool to model this kind of systems. Neverthe predicted S and  $\beta$  values are slightly lower than those obtained from the experimental measurements. This difference between experimental and predicted values is higher for the system containing [EMim]][NTf<sub>2</sub>], which show a larger immiscibility area (low alkane concentration in the IL-rich phase). In this case, a minimal variation in the alkane composition in the IL-rich phase leads to a substantially change of the values of these parameters, especially the S values.

The COSMO-RS model was also applied by Ferreira et al. [40] to describe the phase behavior of the ternary systems reported in this work. Comparing both models, a better description of the phase behavior is obtained using GC-EoS. Although the COSMO-RS model also predicts quite well the trends, a higher deviation between experimental and calculated values was obtained for S and  $\beta$  data. Moreover, the prediction of the binodal curves using the COSMO-RS model is poorer for systems with longer alkyl chains. In addition, the COSMO-RS predicts a ternary diagram of type 1 for the systems containing [BMim][NTf<sub>2</sub>] and [OMim][NTf<sub>2</sub>] ILs, and for which a diagram of type 2 was experimentally observed.

#### 5. Conclusions

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In this work, experimental ELL data for the binary mixtures {benzene (1)+[EMim][NTf<sub>2</sub>] or [Hmim][NTf<sub>2</sub>] (2)} were measured at atmospheric pressure and temperatures between 293.15 K and 333.15 K. The experimental results show that, within this temperature range, the solubility of benzene in both ILs changes very little. On the other hand, solubility increases with the length of the side alkyl chain of the cation.

The GC-EoS equation was applied to model the phase behavior of mixtures of ionic liquids of the homologous families 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide with benzene and n-hexane. The model was applied to calculate VLE and LLE of binary mixtures {benzene +x-MimNTf<sub>2</sub>} and LLE of ternary systems {n-hexane + benzene + x-MimNTf<sub>2</sub>}. The results show that this equation is capable of giving a good representation of the phase behavior of this type of systems.

### Acknowledgments

This work was partially supported by project PEst-371 C/EQB/LA0020/2011, financed by FEDER through COMPETE -372 Programa Operacional Factores de Competitividade and by 373 Fundação para a Ciência e a Tecnologia 📈 FCT – (Portugal). 374 E.J. González is thankful to FCT for his postdoctoral grant 375 (SFRH/BPD/70776/2010). S.B. Bottini and S. Pereda are thank-376 ful to **CONICET**, ANPCyT and Universidad Nacional del Sur for 377 financial support. 378

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